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# THEORETICAL CHEMISTRY INSTITUTE THE UNIVERSITY OF WISCONSIN

COMPARISON OF THE HARTREE-FOCK ORBITAL  
WITH THE FIRST NATURAL SPIN ORBITAL  
FOR TWO-ELECTRON SYSTEMS

by

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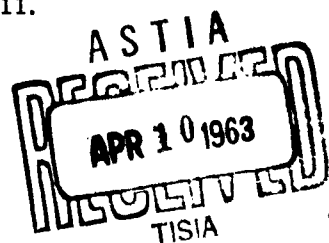
COMPARISON OF THE HARTREE-FOCK ORBITAL WITH THE FIRST  
NATURAL SPIN ORBITAL FOR TWO-ELECTRON SYSTEMS\*

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ABSTRACT

A demonstration is given that for two-electron systems the Hartree-Fock and first natural spin orbitals are different functions. The method used is perturbation theory for which the zero-order problem is the Hartree-Fock approximation. A perturbation expansion through the second order is obtained for the first natural spin orbital. The two orbitals begin to differ in the second order and their energies in the fourth order. An equation for the second order part of the orbital difference function is derived. Estimates of the norms of the orbital difference functions are calculated for the ground states of the helium atom and the hydrogen molecule and are found to be small.



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COMPARISON OF THE HARTREE-FOCK ORBITAL WITH THE FIRST  
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Introduction

Calculations of approximate energies of two-electron systems have shown that the first natural spin orbital gives an approximate energy very close to the Hartree-Fock energy<sup>(1,2,3,4)</sup>. The question has arisen whether the first natural spin orbital would coincide with the Hartree-Fock orbital if it were calculated exactly. One would expect the two orbitals to be different functions because they are defined differently. The Hartree-Fock orbital is defined to give the optimum energy, whereas the first natural spin orbital is defined to have the optimum overlap with the true wave function. In this paper a demonstration is given that the first natural spin orbital is different from the Hartree-Fock orbital for two-electron systems even though the difference is small.

The method followed in this paper is perturbation theory in which the zero-order problem is the Hartree-Fock approximation. The discussion starts with a brief summary of the proof. After that follows a short review of natural spin orbitals for two-electron systems. The perturbation scheme is then defined, and an expression for the first natural spin orbital is developed in terms of the Hartree-Fock orbital. The difference function between the two orbitals is then discussed, and its norm is explicitly calculated for the helium atom.

Throughout the discussion the exact wave function of the two-electron system is always the spatial part of the singlet ground state wave function. Likewise, only the spatial parts of the Hartree-Fock and natural spin orbitals are considered. The spin parts are disregarded since the Hamiltonian does not contain any spin operators.

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- (1) H. Shull and P.-O. Löwdin, J. C. P. 23, 1565 (1955).
- (2) P.-O. Löwdin and H. Shull, Phys. Rev. 101, 1730 (1956).
- (3) H. Shull and P.-O. Löwdin, J. C. P. 30, 617 (1959).
- (4) E. R. Davidson, J. C. P. 37, 2966 (1962).

In brief, the proof that the first natural spin orbital is different from the Hartree-Fock orbital is as follows. The exact wave function of the two-electron system is first expanded in a perturbation series, eq. (12), in which the leading term is the Hartree-Fock function. Then the perturbation expansion of the first natural spin orbital, eq. (14), correct through the second order in the perturbation parameter, is derived. It becomes apparent, eq. (18), that the difference between the two orbitals is not everywhere zero. Therefore the two orbitals are different functions.

The use of perturbation theory is justified by the smallness of the perturbation. An order of magnitude estimate of the perturbation can be obtained from the following considerations. The difference between the Hartree-Fock energy of a two-electron system and the approximate energy given by the first natural spin orbital should be of the fourth order in the perturbation.<sup>(5)</sup> Shull and Löwdin<sup>(3)</sup> found this energy difference to be  $1.43 \times 10^{-4} e^2/a_0$  for the helium atom; Davidson<sup>(4)</sup> obtained  $1.57 \times 10^{-4} e^2/a_0$  for the hydrogen molecule. Therefore, the perturbation is small enough to justify a perturbation expansion.

### Perturbation Expansion of the First Natural Spin Orbital

In this section, a few properties of the natural spin orbitals are first discussed. Then the perturbation scheme which is used in developing the exact wave function of a two-electron system is explicitly stated. After that, the perturbation expansion of the first natural spin orbital is developed.

The exact normalized wave function  $\psi(12)$  of a two-electron system can be expanded in terms of the natural spin orbitals<sup>(2,4,6,7)</sup>  $\chi_k$  as follows:

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(5) See footnote (8).

(6) P.-O. Löwdin, Phys. Rev. 97, 1474 (1955).

(7) E. R. Davidson, J. C. P. 37, 577 (1962).

$$\psi(12) = \sum_{k=1}^{\infty} \eta_k \chi_k(1) \chi_k(2) \quad (1)$$

where the  $\eta_k^2$  are the occupation numbers. The natural spin orbitals are mutually orthonormal, i.e.

$$\int \chi_k^*(1) \chi_{k'}(1) d\tau_1 = \delta_{kk'} \quad (2)$$

For the purposes of this discussion it is convenient to rewrite the wave function  $\psi(12)$  as

$$\psi(12) = \eta_1 \left[ \chi_1(1) \chi_1(2) + T(12) \right] \quad (3)$$

where  $T(12)$  contains all of the natural spin orbitals except the first one. An important property of the first natural spin orbital is that it is strongly orthogonal to the function  $T(12)$ , i.e.

$$\int T^*(12) \chi_1(1) d\tau_1 = \int T^*(12) \chi_1(2) d\tau_2 = 0 \quad (4)$$

The perturbation scheme is obtained by rewriting the exact Hamiltonian  $H$  of the two-electron system as a Hartree-Fock Hamiltonian  $H^{(0)}$  plus a perturbation  $H^{(1)}$

$$H = H^{(0)} + \lambda H^{(1)} \quad (5)$$

where  $\lambda$  is the perturbation parameter which is ultimately set equal to unity. The Hartree-Fock Hamiltonian is

$$H^{(0)} = h^0(1) + h^0(2) \quad (6)$$

where

$$h^0(1) = -\frac{1}{2} \nabla_1^2 - \frac{2}{r_1} + V(1) \quad (7)$$

in atomic units. The Hartree-Fock potential  $V(1)$  in which electron 1 moves is

$$V(1) = \int \phi_o^*(2) \frac{1}{r_{12}} \phi_o(2) d\tau_2 \quad (8)$$

The function  $\phi_o$  is the Hartree-Fock orbital which satisfies the equation

$$h^o(1)\phi_o(1) = \epsilon_o \phi_o(1) \quad (9)$$

with  $\epsilon_o$  as the orbital energy. The Hartree-Fock orbital is normalized to unity, i.e.

$$\int \phi_o^*(1) \phi_o(1) d\tau_1 = 1 \quad (10)$$

The Hartree-Fock function of the two-electron system is given by the product  $\phi_o(1)\phi_o(2)$ . The perturbation term  $H^{(1)}$  in the Hamiltonian is

$$H^{(1)} = \frac{1}{r_{12}} - V(1) - V(2) \quad (11)$$

where  $V$  is defined by eq. (8), and  $r_{12}$  is the inter-electronic distance.

According to the above perturbation scheme the exact wave function  $\psi(12)$  is written as  $\phi_o(1)\phi_o(2)$  plus additional terms. The detailed form of this expansion through the second order in  $\lambda$  is derived in Appendix I, eq. (I,10), and is

$$\begin{aligned} \psi(12) = C \left\{ \phi_o(1)\phi_o(2) + \lambda^2 \left[ \phi_o(1)f^{(2)}(2) + f^{(2)}(1)\phi_o(2) \right] \right. \\ \left. + \lambda s^{(1)}(12) + \lambda^2 s^{(2)}(12) + \text{higher order terms} \right\} \quad (12) \end{aligned}$$

The normalization constant  $C$  is also the overlap between  $\psi(12)$  and the Hartree-Fock function  $\phi_o(1)\phi_o(2)$ . The functions  $f^{(2)}$ ,  $s^{(1)}$



and  $s^{(2)}$  obey the following orthogonality relations (see end of Appendix I),

$$\int f^{(2)*}_{(1)} \phi_o(1) d\tau_1 = 0, \quad (13a)$$

$$\int s^{(1)*}_{(12)} \phi_o(1) d\tau_1 = 0 \quad (13b)$$

and

$$\int s^{(2)*}_{(12)} \phi_o(1) d\tau_1 = 0. \quad (13c)$$

From an examination of  $\psi(12)$  given by eq. (12) it is seen that the second order expansions for the first natural spin orbital and the function  $T(12)$  appearing in eq. (3) are

$$\chi_1(1) = \phi_o(1) + \lambda^2 f^{(2)}_{(1)} \quad (14)$$

and

$$T(12) = \lambda s^{(1)}_{(12)} + \lambda^2 s^{(2)}_{(12)}. \quad (15)$$

The overlap between  $\phi_o(1)$  and  $\chi_1(1)$  is equal to unity, through the second order, since  $\phi_o(1)$  is orthogonal to  $f^{(2)}_{(1)}$ , eq. (13a). Therefore, the overlap  $C$  between  $\psi(12)$  and  $\phi_o(1)\phi_o(2)$  is approximately equal to  $\eta_1$ , the square root of the first occupation number.

The two following observations indicate that eqs. (14) and (15) are the correct second order expansions. First, substituting the two expansions into  $\psi(12)$  given by eq. (3) and keeping terms only through the second order in  $\lambda$  gives the correct form of  $\psi(12)$  through the second order, eq. (12). Second, the perturbation expansion of the first natural spin orbital, eq. (14), satisfies the normalization condition, eq. (2) with  $k = k' = 1$ , through the second order in  $\lambda$ , i.e.

$$\int [\phi_o(1) + \lambda^2 f^{(2)}_{(1)}]^* [\phi_o(1) + \lambda^2 f^{(2)}_{(1)}] d\tau_1 = 1 \quad (16)$$

by virtue of eqs. (10) and (13a). The two expansions also satisfy, through the second order, the strong orthogonality condition, eq. (4), i.e.

$$\int [\lambda s^{(1)}(12) + \lambda^2 s^{(2)}(12)]^* [\phi_0(1) + \lambda^2 f^{(2)}(1)] d\tau_1 = 0 \quad (17)$$

by virtue of eqs. (13b) and (13c). Therefore, it can be concluded that eq. (14) is the correct second order expansion of the first natural spin orbital for a two-electron system.

From eq. (14) it is apparent that the first natural spin orbital  $\chi_1$  is different from the Hartree-Fock orbital  $\phi_0$ . The difference between the two orbitals, up through the second order in  $\lambda$ , is given by the difference function<sup>(8)</sup>  $f^{(2)}$ .

#### The Difference Function $f^{(2)}$

The equation which the difference function  $f^{(2)}$  satisfies (see Appendix II, eq. (II,6)) is

$$\left( h^{(0)}(1) - \epsilon_0 \right) f^{(2)}(1) = E^{(2)} \phi_0(1) - \int s^{(1)*}(12) H^{(1)} \phi_0(2) d\tau_2 \quad (18)$$

where the function  $s^{(1)}$  satisfies the equation

$$\left( H^{(0)} - 2\epsilon_0 \right) s^{(1)}(12) = \left( E^{(1)} - H^{(1)} \right) \phi_0(1) \phi_0(2) \quad (19)$$

The quantities  $E^{(1)}$  and  $E^{(2)}$  are the first and second order energies of the two-electron system and are given by the well-known eqs. (II,3) and (II,5).

From eq. (19) it is apparent that  $s^{(1)}$  is not everywhere zero. Therefore it follows from eq. (18) that the difference function  $f^{(2)}$  is not everywhere zero. Thus, the first natural spin orbital begins to differ from the Hartree-Fock orbital in the second order.

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(8) From eq. (14) one can verify that the Hartree-Fock energy begins to differ from the first natural spin orbital energy in the fourth order. This result is obtained by taking the expectation value of the Hamiltonian  $H$ , eq. (5), with  $\chi_1(1)\chi_1(2)$  and making use of the form of the perturbation  $H^{(1)}$ , eq. (11).

An estimate for  $f^{(2)}$  can be obtained from a sufficiently good approximate two-electron wave function by the following method.<sup>(9)</sup> Multiplying  $\psi(12)$ , eq. (12), by  $\phi_o(2)$ , integrating over the coordinates of electron 2 and taking the orthogonality relations, eqs. (13a), (13b) and (13c), into account, we obtain

$$f^{(2)}(1) \approx \frac{1}{C} \int \psi^*(12) \phi_o(2) d\tau_2 - \phi_o(1) \quad (20)$$

where

$$C = \int \psi^*(12) \phi_o(1) \phi_o(2) d\tau_1 d\tau_2 \quad (21)$$

Equation (20) is an approximation because the formula gives  $f^{(2)}$  plus higher order contributions. The norm of  $f^{(2)}(1)$  in general is defined to be

$$||f^{(2)}|| = \left( \int f^{(2)*}(1) f^{(2)}(1) d\tau_1 \right)^{\frac{1}{2}} \quad (22)$$

In terms of the two-electron wave function of eq. (12),

$$||f^{(2)}|| \approx \left( -1 + \frac{1}{C^2} \int \left[ \int \psi^*(12) \phi_o(2) d\tau_2 \right]^* \left[ \int \psi^*(12) \phi_o(2) d\tau_2 \right] d\tau_1 \right)^{\frac{1}{2}} \quad (23)$$

Equations (21) and (23) were used to obtain an estimate for the norm of  $f^{(2)}$  for the case of the helium atom. The normalized Hylleraas function<sup>(10)</sup>

$$\begin{aligned} \psi(12) = (1.380) & \left[ 1 + (0.3534)u + (0.1282)t^2 - (0.1007)s \right. \\ & \left. + (0.03305)s^2 - (0.03173)u^2 \right] \exp(-1.818s) \end{aligned} \quad (24)$$

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(9) This method, due to O. Sinanoğlu, was communicated to us by D. Tuan.

(10) E. A. Hylleraas, Z. Physik 54, 347 (1929).

was taken as an approximation to the exact helium wave function. The variables  $s$ ,  $t$  and  $u$  are the well-known combinations  $s = (r_1 + r_2)$ ,  $t = (r_1 - r_2)$  and  $u = r_{12}$  where the  $r_1$ ,  $r_2$ , and  $r_{12}$  are expressed in units of  $a_0 = \hbar^2/\mu e^2$  with  $\mu$  being the reduced mass of the helium atom.

The difference function  $f^{(2)}(1)$ , eq. (20) has the form

$$f^{(2)}(1) = \frac{I(1)}{C} - \phi_0(1) \quad (25)$$

where

$$I(1) = \frac{2\pi}{r_1} \int_{r_2=0}^{\infty} dr_2 \int_{r_{12}=|r_1-r_2|}^{r_1+r_2} dr_{12} r_2 r_{12} \psi^{(12)} \phi_0(2) \quad (26)$$

The following analytic approximation<sup>(11)</sup> to  $\phi_0(2)$  was used

$$\phi_0(2) = \frac{(2.968466)}{4\pi} \left[ \exp(-1.455799 r_2) + (2.00) \exp(-0.8734794 r_2) \right] \quad (27)$$

Here  $r_2$  is in units of  $a_0$ . The function  $I(1)$  turned out to be (with  $r_1$  in units of  $a_0$ ):

$$\begin{aligned} I(1) = & \left[ (0.1196) \exp(-1.818 r_1) - (0.1092) \exp(-5.092 r_1) \right. \\ & \left. - (0.01041) \exp(-6.547 r_1) \right] r_1^{-1} + (1.037) \exp(-1.818 r_1) \\ & - (0.08935) \exp(-5.092 r_1) - (0.01231) \exp(-6.547 r_1) \\ & + (0.08650) \exp(-1.818 r_1) r_1 + (0.1286) \exp(-1.818 r_1) r_1^2. \end{aligned} \quad (28)$$

The coefficient  $C$ , eq. (21), is

$$C = 4\pi \int_{r_1=0}^{\infty} dr_1 r_1^2 I(1) \phi_0(1) = 0.9961 \quad (29)$$

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(11) L. C. Green, M. M. Mulder, M. N. Lewis and J. W. Woll, Phys. Rev. 93, 757 (1954).

The norm of  $f^{(2)}$ , eq. (23), is

$$||f^{(2)}|| \approx \left( -1 + \frac{4\pi}{c^2} \int_{r_1=0}^{\infty} dr_1 r_1^2 I(1)I(1) \right)^{\frac{1}{2}} = 0.002 . \quad (30)$$

Thus the norm of  $f^{(2)}$  is very small compared to unity, the norm of  $\varphi_0$ .

The overlap between the Hartree-Fock and first natural spin orbitals, through the fourth order, is

$$\int \varphi_0(1) \chi_1(1) d\tau_1 = \left( 1 + ||f^{(2)}||^2 \right)^{-\frac{1}{2}} = 0.999998 . \quad (31)$$

Our value for the overlap is higher than the value obtained by Löwdin and Shull,<sup>(2)</sup> 0.99995080. Sinanoğlu has mentioned that as one improves an approximate two-electron wave function, the magnitude of the function  $f^{(2)}$  is reduced. Since the energy obtained by Löwdin and Shull is  $-2.8785973 \text{ e}^2/a_0$  as compared with  $-2.90324 \text{ e}^2/a_0$  obtained by Hylleraas,<sup>(10)</sup> the wave function calculated by Löwdin and Shull has a larger  $f^{(2)}$  than the Hylleraas function, eq. (24). Thus, the above overlaps are in the correct relationship.

Davidson<sup>(4)</sup> has examined the natural spin orbital expansion of the Kolos and Roothaan wave function for the hydrogen molecule. He obtained 0.999982 for the overlap between the Hartree-Fock and first natural spin orbitals of  $H_2$ . Therefore, the norm of the  $f^{(2)}$  associated with the Kolos and Roothaan wave function is approximately 0.006. This value is small compared to unity, the norm of the Hartree-Fock function for  $H_2$ .

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## APPENDIX I

## Perturbation Expansion of an Exact Two-Electron Wave Function

In this appendix a derivation is given of the form which an exact two-electron wave function  $\psi(12)$  must necessarily assume if it is developed according to the perturbation scheme described by eqs. (5) through (11).

If the exact two-electron Hamiltonian of the system is decomposed according to eqs. (5) and (6), then the two-electron Schrödinger equation which  $\psi(12)$  satisfies can be written as

$$\left( h^0(1) + h^0(2) + \lambda H^{(1)} \right) \psi(12) = E \psi(12) \quad (I,1)$$

where  $E$  is the exact energy of the two-electron system.

The zero-order two-electron problem associated with eq. (I,1) is

$$\left( h^0(1) + h^0(2) \right) \phi_0(1) \phi_0(2) = 2\epsilon_0 \phi_0(1) \phi_0(2) . \quad (I,2)$$

Therefore  $\psi(12)$  must be written as the solution of the zero-order problem,  $\phi_0(1) \phi_0(2)$ , plus some other functions.

The one-electron problem equivalent to eq. (I,2) is

$$h^0(1) \phi_0(1) = \epsilon_0 \phi_0(1) . \quad (I,3)$$

The one-electron Hamiltonian  $h^0(1)$ , eq. (7), is

$$h^0(1) = -\frac{1}{2} \nabla^2(1) - \frac{2}{r_1} + \int \phi_0^*(2) \frac{1}{r_{12}} \phi_0(2) d\tau_2 \quad (I,4)$$

with the Hartree-Fock potential  $V(1)$ , eq. (8), written out explicitly. It should be noted that the operator  $h^0(1)$  in eqs. (I,1) to (I,4) depends on the unknown function  $\phi_0$ .

After eq. (I,4) is solved for  $\phi_0$ , one can use the operator  $h^0(1)$  with  $\phi_0$  fixed to define the following eigenvalue problem

$$h^0(1) \phi_k(1) = \epsilon_k \phi_k(1) \quad k = 1, 2, \dots . \quad (I,5)$$

The two-electron wave function  $\psi(12)$  can be expanded in terms of products of the form  $\phi_i(1)\phi_j(2)$  where  $i, j = 0, 1, 2, \dots$ . In these products the orbitals are any solution of eq. (I,5) or the Hartree-Fock orbital  $\phi_0$ . Therefore the perturbation expansion of  $\psi(12)$  through the second order in  $\lambda$  is

$$\psi(12) = C \left\{ \phi_0(1)\phi_0(2) + \sum_{i,j=0}^{\infty} \left[ \lambda c_{ij}^{(1)} + \lambda^2 c_{ij}^{(2)} \right] \phi_i(1)\phi_j(2) + \text{higher order terms} \right\} \quad (\text{I},6)$$

where  $C$  is the normalization constant. The summation sign includes integration over the continuum while the asterisk implies that the subscripts  $i$  and  $j$  are never both equal to zero.

The perturbation expansion of eq. (I,1) is obtained by substituting into eq. (I,1)  $\psi(12)$  from eq. (I,6) and  $E$  from the well-known expansion

$$E = 2\epsilon_0 + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots \quad (\text{I},7)$$

Collecting coefficients of  $\lambda$  and  $\lambda^2$  one obtains, respectively, the well-known expressions

$$c_{ij}^{(1)} = \frac{\langle \phi_i(1)\phi_j(2) | E^{(1)} - H^{(1)} | \phi_0(1)\phi_0(2) \rangle}{(\epsilon_i + \epsilon_j - 2\epsilon_0)} \quad (\text{I},8)$$

and

$$c_{ij}^{(2)} = \sum_{m,n=0}^{\infty} \frac{\langle \phi_i(1)\phi_j(2) | E^{(1)} - H^{(1)} | \phi_m(1)\phi_n(2) \rangle}{(\epsilon_i + \epsilon_j - 2\epsilon_0)} \times \frac{\langle \phi_m(1)\phi_n(2) | E^{(1)} - H^{(1)} | \phi_0(1)\phi_0(2) \rangle}{(\epsilon_m + \epsilon_n - 2\epsilon_0)} \quad (\text{I},9)$$

where the brackets are a short-hand notation for the integrals. A straight forward calculation shows that the integrals

$\langle \phi_i^{(1)} \phi_j^{(2)} | \mathbb{E}^{(1)} - H^{(1)} | \phi_0^{(1)} \phi_0^{(2)} \rangle$  vanish if at least one of the subscripts  $i$  or  $j$  is equal to zero.

Substituting eqs. (I,8) and (I,9) into eq. (I,6) one obtains the desired second order expansion of  $\psi(12)$ , namely

$$\begin{aligned} \psi(12) = c \left\{ \phi_0^{(1)} \phi_0^{(2)} + \lambda^2 \left[ f^{(2)}(1) \phi_0^{(2)} + \phi_0^{(1)} f^{(2)}(2) \right] \right. \\ \left. + \lambda s^{(1)}(12) + \lambda^2 s^{(2)}(12) + \text{higher order terms} \right\}. \end{aligned} \quad (\text{I},10)$$

The functions  $f^{(2)}$ ,  $s^{(1)}$  and  $s^{(2)}$  are

$$f^{(2)}(1) = \sum_{i=1}^{\infty} c_{i0}^{(2)} \phi_i^{(1)}, \quad (\text{I},11a)$$

$$s^{(1)}(12) = \sum_{i,j=1}^{\infty} c_{ij}^{(1)} \phi_i^{(1)} \phi_j^{(2)}, \quad (\text{I},11b)$$

and

$$s^{(2)}(12) = \sum_{i,j=1}^{\infty} c_{ij}^{(2)} \phi_i^{(1)} \phi_j^{(2)}. \quad (\text{I},11c)$$

Since the Hartree-Fock orbital  $\phi_0$  is orthogonal to all of the orbitals  $\phi_i$  ( $k = 1, 2, \dots$ ), the above three functions have the orthogonality properties given by eqs. (13a), (13b) and (13c).



## APPENDIX II

Equation for the Difference Function  $f^{(2)}$ 

In this appendix the equation which the second order difference function  $f^{(2)}$  satisfies is developed by straight forward perturbation techniques.

The equation for  $f^{(2)}$  is obtained from the two-particle Schrödinger equation

$$H\psi(12) = E\psi(12) \quad (\text{II},1)$$

by decomposing the Hamiltonian according to eqs. (5) and (6), expanding  $E$  according to eq. (I,7) and writing for  $\psi(12)$  the perturbation expansion given by eq. (12). Equating coefficients of  $\lambda$  and  $\lambda^2$  one obtains, respectively,

$$\left( H^{(0)} - 2\epsilon_0 \right) s^{(1)}(12) = \left( E^{(1)} - H^{(1)} \right) \phi_0(1) \phi_0(2) \quad (\text{II},2)$$

where

$$E^{(1)} = \iint \phi_0^*(1) \phi_0^*(2) H^{(1)} \phi_0(1) \phi_0(2) d\tau_1 d\tau_2 \quad (\text{II},3)$$

and

$$\begin{aligned} \left( H^{(0)} - 2\epsilon_0 \right) \left[ f^{(2)}(1) \phi_0(2) + \phi_0(1) f^{(2)}(2) \right] + \left( H^{(0)} - 2\epsilon_0 \right) s^{(2)}(12) \\ = E^{(2)} \phi_0(1) \phi_0(2) + \left( E^{(1)} - H^{(1)} \right) s^{(1)}(12) \end{aligned} \quad (\text{II},4)$$

where

$$E^{(2)} = \iint s^{(1)*}(12) H^{(1)} \phi_0(1) \phi_0(2) d\tau_1 d\tau_2 \quad (\text{II},5)$$

Multiplying eq. (II,4) by  $\phi_0(2)$ , integrating over electron 2 and taking eqs. (13a), (13b) and (13c) into account, one obtains the equation for the difference function  $f^{(2)}$ , namely

$$\left(h^{(1)} - \epsilon_0\right) f^{(2)}(1) = E^{(2)} \phi_0(1) - \int S^{(1)*}(12) H^{(1)} \phi_0(2) d\tau_2 \quad (\text{II},6)$$

where  $E^{(2)}$  is given by eq. (II,5) and  $S^{(1)}$  satisfies eq. (II,2).